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(54) Title: CHLORINATED POLYVINYL CHLORIDE COMPOUNDS HAVING EXCELLENT COMBUSTION CHARACTERISTICS			
(57) Abstract			
<p>The present invention relates to a chlorinated polyvinyl chloride compound and an article made therefrom. The compound contains less than 40 weight percent inorganic and meets Factory Mutual Test Standard Class Number 4910. The compound exhibits good physical properties, excellent combustion characteristics as well as ease of processability.</p>			

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**CHLORINATED POLYVINYL CHLORIDE COMPOUNDS
HAVING EXCELLENT COMBUSTION CHARACTERISTICS**

5 **FIELD OF INVENTION**

This invention relates to unique thermoplastic compounds having less than 40 weight percent inorganic content and exceptional combustion characteristics. In particular, the invention relates to chlorinated polyvinyl chloride compounds having a low inorganic content which at a minimum meet Factory Mutual Test Standard Class 10 Number 4910 requirements. Furthermore, the invention relates to an article made from this unique compound.

BACKGROUND OF THE INVENTION

Due to the use of thermoplastic materials in various environments, the 15 combustion characteristics of these materials are very important. In one particular environment, clean rooms used in the semiconductor industry, these characteristics are of utmost importance so that if combustion of the thermoplastic material did occur, it would not severely damage the equipment or the contents of the clean room. These characteristics are important in other environments also since the thermoplastic material 20 may possibly spread and propagate the fire, and generate smoke as the combustion occurs. Additionally, the thermoplastic material may emit corrosive materials subject to decomposition by combustion.

Although a few compounds exist which limit fire propagation and smoke and corrosive by products, most of these materials are filled with large amounts of 25 inorganic materials to obtain the desired balance of the combustion characteristics. There still exists a need for a CPVC composition which has low inorganic content, and excellent combustion characteristics, which can be easily processed.

Factory Mutual Test Standard Class Number 4910 sets forth the 30 flammability test protocol. The test according to the standard is performed in a 50 kW Peak Heat Release Rate Apparatus according to the conditions set forth in the standard.

These standard specifications are especially useful for semiconductor clean room materials. It is believed that these standard specifications could be applicable to building codes or any other codes regulating combustible materials. This test standard is incorporated herein in its entirety. This test standard sets forth criteria used in the evaluation of the fire propagation behavior of a material, the possibility for smoke contamination caused by the material as well as the possibility of contamination due to corrosive by products of the combustion of the material. The Factory Mutual Test Standard Class Number 4910 uses three indices to characterize the materials evaluated. The indices are Fire Propagation Ratio ("FPI"), the Smoke Damage Index ("SDI") as well as the Corrosion Damage Index ("CDI").

FPI indicates the propensity of the material to support fire propagation. It is defined as the ratio of the heat flux from the flame of the burning material to the material's response to the heat flux. The flame heat flux is estimated based upon the heat release rate. The limit for the FPI in the Factory Mutual Test Standard Class Number 4910 is $\leq 6 \text{ (m/s}^{1/2}\text{)}/(\text{kW/m})^{2/3}$.

The SDI is used to determine the smoke contamination of the environment during the propagation of a fire. The SDI is determined by multiplying the smoke yield by the FPI. The smoke yield is defined in the standard as the ratio of the total mass of smoke released to the total mass of the material vaporized. The limit for the SDI in the Factory Mutual Test Standard is $\leq 0.40 \text{ (m/s}^{1/2}\text{)}/(\text{kW/m})^{2/3}$.

The CDI is an indicator of the amount of corrosive products released by the combustion of the thermoplastic material. The value for the CDI is obtained by multiplying the average corrosion index by the fire propagation index. The average corrosion index is based upon a specific corrosion constant determined using a Rohrback-Cosasco (RC) 2500 Å modified corrosion probe as described in the Factory Mutual Test Standard Class Number 4910 multiplied by the yield of corrosive products of combustion. The average corrosion index is the average corrosion rate per unit of

concentration of the material vapors. The limit for the CDI in the Factory Mutual Test Standard 4910 is $\leq 1.1 [(\text{m/s}^{1/2})/(\text{kW/m})^{2/3}] [(\text{\AA/min})/(\text{g/m}^3)]$.

All three criteria must be satisfied for a material to be used in clean room facilities. Several materials meet one or two of the three criteria, as shown in Table 2 of the November 1996 Factory Mutual Publication FMRC J.I. 0B0J8.RC, entitled "Flammability of Clean Room Materials". For example, phenolic-80% fiberglass meets the FPI and SDI as well as epoxy-82% fiberglass-phenolic. Both of these materials have a high inorganic content. Only polyether ether ketone and polyvinylidenefluoride meet all three criteria of the Factory Mutual Test Standard 4910.

Thus, there currently exists a need for a thermoplastic composition having a good combustion characteristics. In particular, a need exists for a CPVC compound which at a minimum meets the requirements of Factory Mutual Test 4910 and which is easy to process. More particularly, there exits a need for a CPVC composition which has excellent combustion characteristics, with low levels of inorganic materials.

SUMMARY OF THE INVENTION

The present invention comprises novel CPVC compounds meeting at a minimum the requirements of the Factory Mutual Test Standard Class No. 4910, while maintaining suitable processability, physical properties such as tensile strength, impact resistance and heat distortion, and low inorganic content. In particular, in one embodiment of the present invention, a unique CPVC compound comprises CPVC resin, impact modifiers, tin stabilizer, as well as an acid scavenger. The impact modifiers are chlorinated polyethylene, and an acrylic impact modifier and a methacrylate-butadiene-styrene ("MBS") impact modifier. In another embodiment of the present invention, the unique CPVC compound comprises CPVC resin, PVC resin, impact modifiers and a tin stabilizer.

Another aspect of the invention is an article made from the novel CPVC compounds which has excellent combustion characteristics.

DETAILED DESCRIPTION

One material which could possibly be used to form a compound with excellent combustion characteristics is chlorinated polyvinyl chloride. Chlorinated polyvinyl chloride (CPVC) is known to have excellent high temperature performance
5 characteristics, among other desirable physical properties. Typically, CPVC has an excess of 57% bound chlorine. CPVC is conveniently made by the chlorination of a polymer of vinyl chloride (PVC). Vinyl chloride polymers include both homopolymers and copolymers of vinyl chloride, having a chlorine content of up to 56.7%. The vinyl chloride polymers used in the post chlorination process are obtained by either mass,
10 suspension or emulsion polymerization techniques.

CPVC is obtained by chlorinating homopolymers or copolymers containing less than fifty percent (50%) by weight of one or more copolymerizable comonomers. Preferably, comonomers are not used. However, suitable comonomers include acrylic and methacrylic acids; esters of acrylic and methacrylic acid wherein the ester portion has from 1 to 12 carbons; hydroxyalkyl esters of acrylic and methacrylic acid (for example hydroxymethyl methacrylate, hydroxyethyl acrylate, hydroxyethyl methacrylate and the like); glycidyl ester of acrylic and methacrylic acid (for example glycidyl acrylate, glycidyl methacrylate and the like); alpha,beta-unsaturated dicarboxylic acids and their anhydrides (for example maleic acid, fumaric acid, itaconic
15 acid and the like); acrylamide and methacrylamide; acrylonitrile and methacrylonitrile; maleimides; olefins (for example ethylene, propylene, isobutylene, hexene and the like); vinylidene halide; vinyl esters; vinyl ethers; crosslinking monomers (for example, diallyl phthalate, ethylene glycol dimethacrylate, methylene bis-acrylamide, divinyl ether, allyl silanes and the like).

25 Any post chlorination processes can be used to form CPVC polymer having more than fifty-seven percent (57%) by weight chlorine based upon the total weight of the polymer. Preferably, the CPVC polymer has a chlorine content in the range of about sixty percent (60%) to about seventy four percent (74%) by weight based

upon the total weight of the polymer. The post chlorination processes which can be used include any commercial process or the like such as solution process, fluidized bed process, water slurry process, thermal process or liquid chlorine process or two step process which comprises post chlorinating the vinyl chloride polymer in the presence of 5 a peroxy catalyst during both steps. In as much as the post chlorination processes are known to the art as well as the literature, they will not be discussed in detail here. Rather reference is hereby made to U.S. Patent Nos. 2,996,049; 3,100,762; 4,412,898 3,532,612; 3,506,637; 3,534,013; 3,591,571; 4,049,517; 4,350,798; 4,377,459, 5,216,088 and 5,340,880 which are hereby fully incorporated by reference as to the method of forming 10 CPVC by post chlorinating PVC. The preferred process in forming the CPVC from the PVC is the aqueous suspension process disclosed in U.S. Patent No. 4,412,898.

In addition, blends of various CPVC resins can also be used. In those instances, the CPVC resin can be blended with another CPVC resin in an amount of other resin of about 1% to about 50%. These blends of CPVC can be used so long as the 15 requirements of the Factory Mutual Test Standard Number 4910 are still met and the compound containing the blend has an inorganic content of less than 40 weight percent.

The CPVC used in the invention desirably will have a fused density in the range of approximately 138 to 156 grams /cubic centimeter at 25° Centigrade, an inherent viscosity (I.V.) in the range of about 0.52 to about 1.0 and a chlorine content of 20 at least sixty percent (60%). The preferred fused density of the CPVC is in the range of about 146 to about 156 grams/cubic centimeter. The preferred inherent viscosity is in the range of about 0.68 to about 0.92. The preferred chlorine content of the CPVC is about 63 % to about 68 %. The most preferred chlorine content is 67%, with a 0.68 I.V. and a fused density of 1.53 grams/cubic centimeter. Examples of suitable CPVC to use in 25 forming the compound of the instant invention include TempRite 677x 670 CPVC, and TempRite 674x571 CPVC, all available from The B.F. Goodrich Company. TempRite is a registered trademark of The B.F.Goodrich Company. The most preferred CPVC resin is TempRite 677x670 CPVC.

In one embodiment of the instant invention, the CPVC is formed into a compound with chlorinated polyethylene, acrylic impact modifier, a MBS impact modifier, a tin stabilizer and an acid scavenger.

The chlorinated polyethylene (CPE) used in the compound of the first embodiment is a rubbery material resulting from the chlorination of polyethylene having a substantially linear structure. The polyethylene can be chlorinated by various methods including aqueous suspension, solution or gas phase methods. An example of a method for preparing CPE can be found in U.S. Patent No. 3,563,974. Preferably, the aqueous suspension method is used to form the CPE. Generally to be used as an impact modifier, the CPE material contains from 5 to 50% by weight of chlorine. Preferably, the CPE contains from 25 to 45 % by weight of chlorine. CPE is commercially available from The Dow Chemical Company. The preferred CPE materials to be used in the compound include Tyrin 3611P, Tyrin 2000 and Tyrin 3615P; all available from the Dow Chemical Company. Tyrin is a trademark of the Dow Chemical Company. The most preferred CPE material is Tyrin 3611P, from the Dow Chemical Company. Additionally, the CPE can comprise a mixture of chlorinated polyethylenes, provided that the overall mixture has a chlorine content in the range of about 25 to 45% by weight chlorine. The CPE is added to CPVC of the compound of the instant invention in the range of from about 1 to 10 parts per hundred parts of CPVC resin. Preferably, the amount of CPE added to the compound is 2.5 to 7.0 parts per 100 parts of the CPVC resin. Most preferably, the amount of CPE added to the compound is 2.0 parts per 100 parts of the CPVC resin.

In addition to the CPVC, and CPE, the first embodiment of the instant invention also includes a acrylic impact modifiers. U.S. Patent No. 3,678,133 describes the compositions conventionally referred to as acrylic impact modifiers. Generally, the acrylic impact modifier is a composite interpolymer comprising a multi-phase acrylic base material comprising a first elastomeric phase polymerized from a monomer mix comprising at least 50 wt.% alkyl methacrylate having 1-4 carbon atoms in the alkyl group and having a molecular weight of from 50,000 to 600,000. Further, the patent

states that the polymerization of the rigid thermoplastic phase is preferably conducted in such a fashion that substantially all of the rigid phase material is formed on or near the surface of the elastomeric phase. Acrylic impact modifiers are polyacrylates including (C₄- C₁₂) acrylate homo or copolymers, second stage graft copolymerized with methyl methacrylate and styrene, poly(ethylhexyl acrylate-co-butyl-acrylate) graft copolymerized with styrene, and/or acrylonitrile and/or methyl methacrylate; polybutyl acrylate graft polymerized with acrylonitrile and styrene. Examples of suitable acrylic impact modifiers include Paraloid EXL-2330, KM 330, KM 334, and KM 365; all of which are available from Rohm and Haas. Paraloid is a trademark of the Rohm & Haas Company. Other commercially available acrylic impact modifiers include Blendex 975, 977 or 979; all available from GE Plastics. Blendex is a trademark of GE Plastics. Additionally Durastrength 200, available from ATO and FM-10 and FM-25, available from Kaneka, are examples of commercially available acrylic impact modifiers. The acrylic impact modifiers are added to CPVC of the compound of the instant invention in the range of from about 1 to 10 parts per hundred parts of CPVC resin. Preferably, the amount of acrylic impact modifier added to the compound is 1.0 to 5.0 parts per 100 parts of the CPVC resin. Most preferably, the acrylic impact modifier is added in 2.0 parts per 100 parts of CPVC resin.

MBS impact modifiers are graft polymers. Generally, MBS impact modifiers are prepared by polymerizing methyl methacrylate or mixtures of methyl methacrylate with other monomers in the presence of polybutadiene or polybutadiene-styrene rubbers. Further information on MBS impact modifiers can be found in the Second Edition of the Encyclopedia of PVC, edited by Leonard I. Nass, Marcel Dekker, Inc. (N.Y. 1988, pp.448-452). Preferably, the amount of MBS impact modifier added to the CPVC of the compound of the instant invention is in the range of 1.0 to 10.0 parts per 100 parts of CPVC resin. Examples of commercially available MBS impact modifiers include Paraloid KM 680, available from Rohm & Haas, Kane Ace B-22 impact modifier and Kane Ace B-56 impact modifier available from Kaneka. The most preferred MBS

impact modifier is Paraloid KM 680. If used in the composition of the first embodiment, 5 parts of the MBS impact modifier are added.

The tin stabilizer used in the present invention can be any stabilizer containing tin. Suitable stabilizers include tin salts of monocarboxylic acids such as stannous maleate. Additionally, organo-tin stabilizers such as dialkyl tin mercaptides, carboxylates, and thiazoles can be used. Examples of such organo-tin stabilizers include without limitation: dibutyltin dilaurate, dibutyltin maleate, di(n-octyl) tin maleate, dibutyl tin bis(2-ethylhexyl mercaptoacetate), dibutyltin bis(lauryl mercaptide), dibutyltin, S,S-bis(isooctyl thioglycoate), dibutyltin β -mercaptopropionate, di-n-octyltin S,S-bis(isooctyl thioglycolate), and di-n-octyltin β -mercaptopropionate. Usually from about 1 to about 5 parts by weight of tin stabilizer per 100 parts of CPVC resin is used in the composition. Preferably, the composition uses between 2 and 4 parts by weight of dibutyl tin bis(2-ethylhexyl mercaptoacetate) per 100 parts of the CPVC resin. Most preferably, 3.5 parts by weight of tin stabilizer per 100 parts of CPVC resin are used.

Examples of a commercially available tin stabilizer are Mark 292-S stabilizer from Witco Chemical and Thermolite 31HF stabilizer from Elf Atochem.

In the first embodiment of the novel compound of the instant invention, an acid scavenger is added to the composition. The acid scavenger is any generated reactive ingredient which can react with any acid formed by the decomposition of the novel CPVC compound of the instant invention. Examples of suitable acid scavengers include metal salts such as carbonates. More specifically, an example of a suitable metal salt includes calcium carbonate. An example of a commercially available calcium carbonate is Ultraflex H, available from Specialty Chemical. Preferably, the acid scavenger is used in the amount of 0.5 to 10 parts per 100 parts of CPVC resin. Most preferably, 0.5 parts of the acid scavenger are used in the compound of the instant invention.

It is believed, that the acid scavenger can be used to improve the combustion characteristics of any halohydrocarbon polymers. Examples of polymers

which could be compounded with the acid scavenger include polyvinyl chloride, chlorinated olefins such as chlorinated polyethylene, halogenated styrenics, and so forth. It is believed that the acid scavenger would react with the halogen released upon the decomposition of the halohydrocarbon polymer. It is believed that the addition of the acid scavenger to such a polymer would reduce the amount of smoke and corrosive materials generated during combustion and thus improve the combustion characteristics of the halogenated polymer.

In the second embodiment of the instant invention, a novel CPVC compound is obtained by the mixture of a CPVC, a PVC, tin stabilizer and a acrylic impact modifier and a MBS impact modifier. The CPVC, tin stabilizer and the acrylic impact modifier and the MBS impact modifier were described above in conjunction with the first embodiment of the invention. In addition to these ingredients, 50 parts of PVC per 50 parts of CPVC are added to the compound. The PVC used in the blend has an inherent viscosity in the range of 0.52 to 1.0; a fused density of about 1.35 grams/cubic centimeter and a chlorine content of about 56.7%. The PVC polymers can be homopolymers or copolymers of polyvinylchloride. Copolymers of PVC are formed predominately with PVC and other copolymers such as for example vinyl acetate. Generally, the secondary monomer is present in the range of five percent. A further discussion of PVC copolymers can be found in Volume 1 of Encyclopedia of PVC, edited by Leonard I. Nass, Marcel Dekker, Inc. (N.Y. 1976, Chap.4). Examples of suitable PVC polymers include Geon 110x 440 PVC from the Geon Company. In the most preferred embodiment, 20 parts of the PVC are added for every 80 parts of CPVC in the compound. Additionally, 10 parts of the MBS impact modifier are included in the composition.

Additives can also be added to the unique CPVC compounds as needed. Conventional additives known in the art as well any other additives may be used, provided that the additive does not alter the combustion characteristics and the processability associated with the novel compounds. Examples of additives which can be

used include antioxidants, lubricants, stabilizers, other impact modifiers, pigments, glass transition enhancing additives, processing aids, fusion aids, fillers, fibrous reinforcing agents and antistatic agents.

Exemplary lubricants are polyglycerols of di- and trioleates, polyolefins such as polyethylene, polypropylene and oxidized polyolefins such as oxidized polyethylene and high molecular weight paraffin waxes. Since several lubricants can be combined in countless variations, the total amount of lubricant can vary from application to application. Optimization of the particular lubricant composition is not within the scope of the present invention and can be determined easily by one of ordinary skill in the art. Preferably, an oxidized polyethylene is used. An example of an oxidized polyethylene is AC 629A, sold by Allied Signal. In addition to the oxidized polyethylene, preferably a paraffin wax is also included in the compounds of the instant invention. An example of a paraffin wax is Paraffin 160F Prill from Witco. Lubricants can be used in the amount of about 0.01 to about 5 parts by weight of lubricant per 100 parts of the CPVC resin. Preferably from about 0.4 to about 2.0 parts by weight of lubricant per 100 parts of CPVC resin are used. In the most preferred embodiment, 1.25 parts by weight of polyethylene and 1.25 parts of paraffin wax are used per 100 parts of CPVC resin.

Co-stabilizers may be included, if desired, but are not necessary.

However, if a solid co-stabilizer is added, the particle size of the co-stabilizer must be small enough so as not to affect the impact properties of the unique compound. Examples of co-stabilizers include metal salts of phosphoric acid, polyols, epoxidized oils, and acid acceptors which are not detrimental to the base CPVC resin used. The stabilizers can be used by themselves or in any combination as desired. Specific examples of metal salts of phosphoric acid include water-soluble, alkali metal phosphate salts, disodium hydrogen phosphate, orthophosphates such as mono-, di-, and tri-orthophosphates of said alkali metals, alkali metal polyphosphates, -tetrapolyphosphates and -metaphosphates and the like. Polyols such as sugar alcohols, and epoxides such as

epoxidized soya oil can be used. Examples of possible acid acceptors include potassium citrate, aluminum magnesium hydroxy carbonate hydrate, magnesium aluminum silicates and alkali metal alumino silicates. An example of commercially available aluminum magnesium hydroxy carbonate hydrate is Hysafe 510, available from the J.M. Huber Company. Examples of magnesium aluminum silicates are molecular sieves, whereas examples of alkali metal alumino silicates are zeolites. The most preferred co-stabilizer, if used at all, is disodium hydrogen phosphate (DSP) and is used by treating the CPVC resin itself, after the resin has been chlorinated. Typical levels of co-stabilizers can range from about 0.1 weight parts to about 7.0 weight parts per 100 weight parts of the CPVC resin, if used at all. DSP is commercially available from The Monsanto Company.

Suitable processing aids include acrylic polymers such as methyl acrylate copolymers. Examples of process aids include Paraloid K 120ND, K-120N, K-175; all available from Rohm & Haas. A description of other types of processing aids which can be used in the compound can be found in The Plastics and Rubber Institute: International Conference on PVC Processing, April 26-28 (1983), Paper No. 17. In some embodiments, no processing aid is necessary, but if used, the processing aid should be used in the amount of 0.5 to about 2.0 by weight of processing aid per 100 parts of the CPVC Resin.

Examples of antioxidants to be used in the compound include Irganox 20 1010 (tetrakis[methylene(3,5-di-tert-butyl-4-hydroxy-hydrocinnamate)]methane) sold by Ciba Geigy. The antioxidant is used in the amount of about 0.1 to about 1.0 parts by weight per 100 parts of the CPVC resin, if used at all.

Suitable pigments include among others titanium dioxide, and carbon black. If included, the pigments are used generally in the amount of about 0.5 to about 25 12.0 parts by weight per 100 parts of the CPVC resin. The preferred titanium dioxide is Tiona RCL-6 from SCM Pigments. The preferred carbon black is Raven 410 , available from Columbian Chemicals.

Suitable inorganic fillers include talc, clay, mica, wollastonite, silicas, and other filling agents. If used in the novel compound having exceptional combustion characteristics, the amount of filler used is less than 40 weight percent. More preferably, the amount of the filler is in the range of about 0.1 to about 12 parts by weight of filler per 100 parts of the CPVC resin.

The components of the unique CPVC compound can be made in any manner wherein the various components are added together and mixed under heat. For example, the appropriate amount of the CPVC resin can be added to a vessel such as Henschel mixer or a ribbon blender. The remaining ingredients of the compound can then be added thereto and mixed. If pellets are to be formed, the compound can be melt mixed. Melt mixing can generally occur in the temperature range of about 150 to about 250° C. Once the blend is formed, it can be processed further depending upon the desired application in any conventional manner, using extrusion or molding techniques.

If extrusion techniques are used to process the composition of the present invention, generally conventional extrusion machinery such as a multi-screw extruder or a single screw extruder are used. An extruder generally has conveying means, an intermediate screw processing means and a final die through which the material is discharged in the form of an extrudate. Generally, a multi-screw extruder is used for the extrusion of pipe. Examples of possible conventional extruders to be used to process the CPVC compound of the instant invention include the following twin screw counterrotating extruder models from Cincinnati Milacron: CM 35HP, CM 55HP, CM 65HP, CM 80HP, CM 92HP. Examples of suitable conical twin screw extruders from Krauss Maffei include KMD-2/ 40KK and KMD-2/50KK.

Once the CPVC compound is made according to the instant invention, it can be formed into any article desired. These articles will have excellent combustion characteristics and will meet Factory Mutual Test Standard Class Number 4910. Examples include but are not limited to sheet, pipe, ducts, fittings, valves, injection

molded and thermoformed industrial parts, appliance housing, fabricated parts, and different containers.

The following non-limiting examples serve to further illustrate the present invention in greater detail.

5

EXAMPLES

In the first example, the CPVC compound utilizing an acid scavenger is formed. The second example shows the recipe for the second embodiment of the invention. Comparative Example 1 is a recipe for a conventional compound.

Ingredients	Ex.1	Ex.2	Comp. Ex.1
TempRite 677x670 CPVC (BFGoodrich)	100	80	100
Geon 110 x440 PVC (The Geon Co.)	----	20	----
Mark 292-S Tin (Witco Chemical)	3.5	3.5	3.5
Paraloid KM 330 Acrylic Impact Modifier (Rohm & Haas)	2.0	2.0	2.0
Paraloid KM 680 MBS Impact Modifier (Rohm & Haas)	5.0	10.0	5.0
Tiona RCL-6 Titanium Dioxide (SCM Pigments.)	12.0	5.0	5.0
AC 629A Polyethylene (Allied Signal)	1.25	1.25	1.25
Paraffin 160 F Prill Wax (Witco Chemical)	1.25	1.25	1.25
Raven 410 Carbon Black	----	0.2	0.2
Tyrin 3611P Chlorinated Polyethylene (Dow)	2.0	----	----
Ultraflex H Calcium Carbonate	0.5	----	----

The above listed compounds were mixed using a Farrel 2 rotor intensive mixer, Model 00C, flexed and dropped at 405° F. The material was sheeted on a KSBI two roll 10 in. x 20 in. mill, Model 6026-DX at 410 ° F. The slabs were removed and compression molded into plaques under the following conditions using a Wabash Steam and Electric Press, Model V752H-15DCLX. A press cycle was conducted for 5 minutes, with a 5 minute preheat cycle under pressure (405 ° F, and 1500 psi.) The samples were then subject to the Clean Room Material Flammability Test Protocol in the Factory Mutual Test Standard Class Number 4910.

Test Results	Ex.1	Ex.2	Comp. Ex.1
Critical Heat Flux (kW/m^2)	20	8	
Thermal Response Parameter ($\text{kW}\cdot\text{s}^{1/2}/\text{m}^2$)	1476	1044	
Fire Propagation Index ($\text{m}/\text{s}^{1/2}$)/ $(\text{kW}/\text{m})^{2/3}$	2	2	5*
Corrosion Index ($\text{\AA}/\text{min}$)/(g/m^3)	0.32	0.28	0.465
Smoke Yield (g/g)	0.015	0.031	
SDI (g/g) $(\text{m}/\text{s}^{1/2})$ / $(\text{kW}/\text{m})^{2/3}$	0.030	0.062	0.044
CDI [$(\text{m}/\text{s}^{1/2})$ / $(\text{kW}/\text{m})^{2/3}$][($\text{\AA}/\text{min}$)/(g/m^3)]	0.64	0.56	2.3

* This value is the value assigned by Factory Mutual and is not based upon actual test results.

The results of these experiments show that the new compounds of the instant invention which have low organic content meet the tests of the Factory Mutual Test Standard Class Number 4910. The conventional CPVC compound did not meet the test. These results also show that these compounds have excellent combustion characteristics and could be used in materials for clean room applications.

In summary, novel and unobvious CPVC compounds have been described as well as an article made from such compounds. Although specific embodiments and examples have been disclosed herein, it should be borne in mind that these have been provided by way of explanation and illustration and the present invention is not limited thereby. Certainly modifications which are within the ordinary skill in the art are considered to lie within the scope of this invention as defined by the following claims.

We claim:

1. A compound having low inorganic content comprising chlorinated polyvinyl chloride, a tin stabilizer, acrylic impact modifier, methacrylate-butadiene-styrene impact modifier, chlorinated polyethylene, and an acid scavenger.
- 5 2. A compound according to claim 1, wherein said chlorinated polyethylene is found in the range from about 2.5 to about 7.0 parts by weight per 100 parts by weight of said chlorinated polyvinyl chloride resin.
- 10 3. A compound according to claim 1, wherein said acrylic impact modifier is found in the range of about 1.0 to about 5.0 parts by weight per 100 parts by weight of said CPVC resin.
4. A compound according to claim 1, wherein said methacrylate-butadiene-styrene impact modifier is found in the range of about 1.0 to about 10.0 parts by weight per 100 parts by weight of said CPVC resin.
- 15 5. A compound according to claim 1, wherein said tin stabilizer is found in the range of from 1.0 to 5.0 parts per weight per 100 parts by weight of said chlorinated polyvinyl chloride resin.
6. A compound according to claim 1, wherein said compound meets or exceeds the requirements of Factory Mutual Test Standard Class Number 4910 .
- 20 7. A compound formed according to claim 1, comprising a 100 parts of said chlorinated polyvinyl chloride resin having a chlorine content of 67%, 2.0 parts of said chlorinated polyethylene and 2.0 parts of said an acrylic impact modifiers, and 5.0 parts of a methacrylate-butadiene-styrene impact modifier.
8. A compound according to claim 1 formed into an article.
- 25 9. A compound according to claim 1, wherein said acid scavenger is calcium carbonate.
10. An article formed from chlorinated polyvinyl chloride compound which meets or exceeds Factory Mutual Test Standard Class Number 4910.

11. A compound comprising 1 to 50 parts of chlorinated polyvinyl chloride, 1 to 50 parts by weight of polyvinyl chloride, 1 to 5 parts of tin stabilizer, 1 to 10 parts by weight of acrylic impact modifiers and 1 to 10 parts by weight of a methacrylate-butadiene-styrene impact modifier.

5 12. A compound according to claim 11, wherein said compound meets or exceeds the requirements of Factory Mutual Test Standard Class Number 4910 .

13. A compound having low inorganic content that meets or exceeds the requirements of Factory Mutual Test Standard 4910 comprising chlorinated polyvinyl chloride, a stabilizer, impact modifier and a processing aid.

10 14. A compound according to claim 13 wherein said stabilizer is a tin stabilizer.

15. A compound according to claim 14, wherein said stabilizer is found in the range of from about 1 part to about 5 parts per weight per 100 parts by weight of chlorinated polyvinyl chloride.

16. A compound according to claim 13, wherein said impact modifier is found in the range of from 0.5 to 10.0 parts by weight per 100 parts by weight of chlorinated polyvinyl chloride.

17. A compound according to claim 16, wherein said impact modifier is chosen from the group consisting of acrylic impact modifiers, methacrylate butadiene styrene impact modifiers or mixtures thereof.

20 18. A compound according to claim 13, wherein said processing aid is found in the range of about 0.5 to about 10 parts by weight per 100 parts by weight of chlorinated polyvinyl chloride.

25 19. A compound according to claim 18, wherein said processing aid is chosen from the group consisting of chlorinated polyethylene, low molecular weight paraffin wax or mixtures thereof.

20. A compound according to claim 13, further comprising a filler, wherein said filler is found in the range of about 1 to about 20 parts by weight per 100 parts by weight of said chlorinated polyvinyl chloride.

21. A compound according to claim 20, wherein said filler is titanium dioxide.
22. A compound according to claim 20, wherein said filler is an acid scavenger.
23. A compound according to claim 22, wherein said acid scavenger is calcium carbonate.

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: CHLORINATED POLYVINYL CHLORIDE COMPOUNDS HAVING EXCELLENT COMBUSTION CHARACTERISTICS

(57) Abstract

The present invention relates to a chlorinated polyvinyl chloride compound and an article made therefrom. The compound contains less than 40 weight percent inorganic and meets Factory Mutual Test Standard Class Number 4910. The compound exhibits good physical properties, excellent combustion characteristics as well as ease of processability.

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5:57)

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INTERNATIONAL SEARCH REPORT

Int'l. Appl. No
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A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C08L27/24 C08K13/02 // (C08L27/24, 23:28, 51:00, 51:06), (C08L27/24, 27:06, 51:00, 51:06), (C08K13/02, 3:26, 5:57)		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
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Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 708 143 A (SEKISUI AMERICA CORP) 24 April 1996 (1996-04-24) page 13, line 52 - line 57; claims; examples ---	1-9
A	EP 0 695 782 A (GOODRICH CO B F) 7 February 1996 (1996-02-07) page 3, line 36 - line 40; claims; examples 15,23 ---	1
A	EP 0 568 922 A (GOODRICH CO B F) 10 November 1993 (1993-11-10) claims; examples ---	1-9 -/-
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.		<input checked="" type="checkbox"/> Patent family members are listed in annex.
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Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentstaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer DE LOS ARCOS, E

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>CHEMICAL ABSTRACTS, vol. 119, no. 26, 27 December 1993 (1993-12-27) Columbus, Ohio, US; abstract no. 272687, KATO, MASAHIRO ET AL: "Chlorinated vinyl chloride polymer compositions" XP002130039 abstract & JP 05 222261 A (SEKISUI CHEMICAL CO LTD, JAPAN) 31 August 1993 (1993-08-31)</p> <p>---</p>	1
A	<p>EP 0 512 610 A (GOODRICH CO B F) 11 November 1992 (1992-11-11) page 2, line 26 - line 31; claims; examples 1-6,9-15</p> <p>-----</p>	1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 99/22881

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
2. Claims Nos.: 10 because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

see further information PCT/isa/210

3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-9

Remark on Protest

- The additional search fees were accompanied by the applicant's protest.
- No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box 3.

Claims Nos.: 10

The subject-matter of independent claim 10 fails to define the technical features on which a Search Report could be based, since it merely refers to a problem to be solved but not to the features which will constitute the solution to said problem (Art. 17(2)a(ii) and (b)).

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-9

Compound comprising chlorinated polyvinyl chloride, tin stabilizer, acrylic impact modifier, methacrylate-butadiene-styrene impact modifier, chlorinated polyethylene and acid scavenger.

2. Claims: 11-12

Compound comprising chlorinated polyvinyl chloride, polyvinyl chloride, tin stabilizer, acrylic impact modifiers and methacrylate-butadiene-styrene impact modifier.

3. Claims: 13-23

Compound comprising chlorinated polyvinyl chloride, polyvinyl chloride, a stabilizer, impact modifier and processing aid.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 99/22881

Patent document cited in search report	Publication date	Patent family member(s)			Publication date
EP 0708143	A 24-04-1996	CA 2132599 A	DE 69422519 D	JP 8176386 A	13-03-1996 10-02-2000 09-07-1996
EP 0695782	A 07-02-1996	AT 173486 T	DE 69506048 D	DE 69506048 T	15-12-1998 24-12-1998 15-07-1999
		JP 8100097 A	US 5969045 A		16-04-1996 19-10-1999
EP 0568922	A 10-11-1993	CA 2095264 A	JP 6200102 A		05-11-1993 19-07-1994
JP 5222261	A 31-08-1993	NONE			
EP 0512610	A 11-11-1992	US 5274043 A	AT 134683 T	AU 1526592 A	28-12-1993 15-03-1996 12-11-1992
		CA 2067417 A	DE 69208511 D	DE 69208511 T	10-11-1992 04-04-1996 29-08-1996
		DK 512610 T	ES 2086634 T	JP 5132602 A	18-03-1996 01-07-1996 28-05-1993
		MX 9202127 A	NO 921716 A	US 5354812 A	01-11-1992 10-11-1992 11-10-1994